

SPINEL FERRITES NANOPARTICLES FOR ALLOY STEEL PROTECTIVE LAYERS

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Abstract

Covering layers might have very important role in improving performance of many mechanical parts. These layers are usually designed to protect a substrate from the environment and enhance mechanical properties such as hardness. Blackening is a classical approach that is very demanding on resources. This process is based on the alkalisation of surface atoms and the transformation of formed hydroxides to oxides. Such an approach inspired us to carry out experiments resulting in preparation of protective layers with similar properties, by using stoichiometric spinel ferrite nanoparticles (MeFe_2O_4). Thus mechanical parts were covered with ferrite nanoparticles and heated in a furnace. Ferrite samples, which were used as precursor for the preparation of layers, were analysed with X-ray powder diffraction, energy dispersive X-ray spectroscopy and ^{57}Fe Mössbauer spectroscopy. The samples were analysed with ultrasonic hardness test, electron microscopy, and Mössbauer spectroscopy. The protection layers showed a higher hardness compared to untreated parts.

Keywords: Spinel ferrites, protective layer, Mössbauer spectroscopy, hardness test

1. INTRODUCTION

Spinel ferrites are a family of compounds similar to magnetic iron oxides, thus chemically magnetite can be considered as a spinel ferrite. The chemical formula of spinel ferrites is MeFe_2O_4 , where Me is a divalent metal cation, e.g. Zn, Mg, Ni or Mn [1]. If the metal cation does not have a trivalent state, we can presume that the compound has high chemical stability. Spinel ferrites exist in normal, inverse or mixed modification. Both spinel modifications have the same $Fd-3m$ space group, but the distribution of cations can be determined by low temperature Mössbauer spectroscopy [2]. The physico-chemical properties of spinel ferrites are very convenient for passivation of surfaces, long lasting sensors, supercapacitors or contrast agents [1]. Thus the synthetic procedure is the key to tailor nanoparticles for specific purposes. The coprecipitation technique is very convenient for environmentally friendly synthesis of narrowly distributed nanoparticles [3], so it was employed in the study.

A surface treatment of mechanical parts is crucial to fabricate high quality products. Many metals lack rust resistance. Commonly used techniques are able to improve only the mechanical or chemical properties, e.g. galvanisation or painting. Other techniques are able to improve both mechanical and chemical properties, but require a relatively high amount of energy and resources, namely nitriding, anodising or blackening [4]. Blackening is a powerful technique to improve surface properties, hardness and chemical stability [5]. This process is applied to carbon steel such as high quality alloy steel used for guns. Military standards also mention blackening for surface treatment and testing of chemical resistance to moisture, salts and operating fluids (e.g. oil, gasoline). Blackening consists of submerging the part into highly alkaline solution with a high temperature. Leading to the formation of a hydroxide on the surface, which is then heated to form an oxide layer, which is chemically stable. This process is transformed into deposition of spinel ferrite nanoparticles and heating in a furnace for moderate temperature and time.

The goal of the study is to investigate the influence of depositing zinc ferrite nanoparticles on the surface of an alloy steel plate. Basic properties of the prepared zinc ferrite nanoparticles were obtained with X-ray powder diffraction, Mössbauer spectroscopy and scanning electron microscopy. The phase composition of covered alloy steel plate was determined via the same analytical tools. The hardness is the main feature of prepared samples as the only mechanical property investigated during the study.

2. MATERIALS AND METHODS

2.1. Preparation of spinel ferrite nanoparticles

FeCl₃·6H₂O, ZnCl₂ and NaOH (pure analytically) chemicals were purchased from PENTA, s.r.o. (Prague, Czech Republic). Ethanol was purchased from the company Verkon. Nanoparticles were prepared by precipitation of Zn²⁺ and Fe³⁺ ions by sodium hydroxide. The amount of ions were $n(\text{Fe}^{3+}) = 2$ mmol, $n(\text{Zn}^{2+}) = 1$ mmol and $n(\text{OH}^-) = 9$ mmol. The admixture was homogenised for 5 min, then washed by deionised water. Finally, vacuum filtration was applied to collect the precipitate.

2.2. Surface treatment of CL20ES plates

CL20ES is an austenitic stainless steel powder of the chemical composition indicated in **Table 1**. The powder was sintered with a laser to form 25 mm x 25 mm x 3 mm metallic plate. This plate was then thermally treated and finally the plate was sandblasted by corundum abrasive of grain size of 70 - 150 µm. The prepared nanoparticles were dispersed in ethanol and deposited on the plate, then the dispersions were dried at 80 °C and finally the plates were heated in a furnace at the desired temperature for 2 h. Sample Zn_Et_200 was heated at 200 °C and sample Zn_Et_400 was heated at 400 °C.

Table 1 The chemical composition of CL20ES powder

Component	Fe	Cr	Ni	Mo	Mn	Si	P	C, S
Indicative value (%)	Balance	16.5-18.5	10.0-13.0	2.0-2.5	0.0-2.0	≤1.0	≤0.045	≤0.030

2.3. X-ray diffraction (XRD)

X-ray powder diffraction (XRD) was used to determine the crystal structure and phase composition. The measurements were conducted using a Bruker D8 ADVANCE powder diffractometer operating in the Bragg-Brentano parafocusing geometry. The diffractometer was equipped with a LYNXEYE position sensitive detector and with a Co "Kalpha" radiation source. In addition, the divergence slit and Soller slits for the primary beam and the Fe "Kbeta" filter and Soller slits for the secondary beam were applied for the measurements.

2.4. ⁵⁷Fe Mössbauer spectroscopy

To distinguish positions and chemical states of ⁵⁷Fe within the crystal structure in the samples, two Mössbauer spectrometers were used. The first spectrometer is a MS96 transmission Mössbauer spectrometer, the second a Conversion Electron Mössbauer Spectrometer (CEMS). Both operate in constant acceleration mode and make use of a ⁵⁷Co radioactive source in a Rh matrix. Samples were measured at room temperature [6]. The MS96 spectrometer was calibrated using a α-Fe calibration foil zeroing the isomer shift values. No external magnetic field was applied during measurement. The samples were measured at room temperature without applying an external magnetic field. MossWin 4.0 software was used for spectra evaluation [7].

The CEMS works in a reflective geometry and measures a Mössbauer spectrum based on conversion electrons which come from a depth up to 300 nm in the sample [8]. The CEMS makes use of a ФЭУ-85 photomultiplier as its detector. It is build into a Pfeiffer Vacuum Chamber to make the mean free path of the

conversion electrons longer and an electric field is created using an Ortec 556H High Voltage Power Supply between the detector and the sample to accelerate electrons towards the photomultiplier tube.

2.5. Ultrasonic hardness test

Hardness tests were performed with a ultrasonic portable hardness tester MET-U1A (Centre “MET”, Russia). The tester is equipped with a probe that operates according to the ultrasonic contact impedance method (ASTM A 1038, DIN 50159). The hardness was measured on each side several times and an estimated hardness was used to calculate the improvement in hardness as a percentage.

2.6. Energy dispersive X-ray spectroscopy

VEGA3 LMU (TESCAN, Czech Republic) was used to collect EDS spectra, equipped with Si(Li) XFlash 410 EDS detector (Bruker, Germany). The primary energy of electrons was 30 keV with a takeoff angle of 35°.

3. RESULTS

3.1. Zinc ferrite characterisation

Zinc ferrite was synthesised as described in the experimental section. XRD pattern corresponds to *Fd-3m* space group, which is associated with spinel structure, because spinel ferrites have the same space group varying per cell parameter. The recognised peaks correspond exclusively to *Fd-3m* space group pattern (**Figure 1a**).

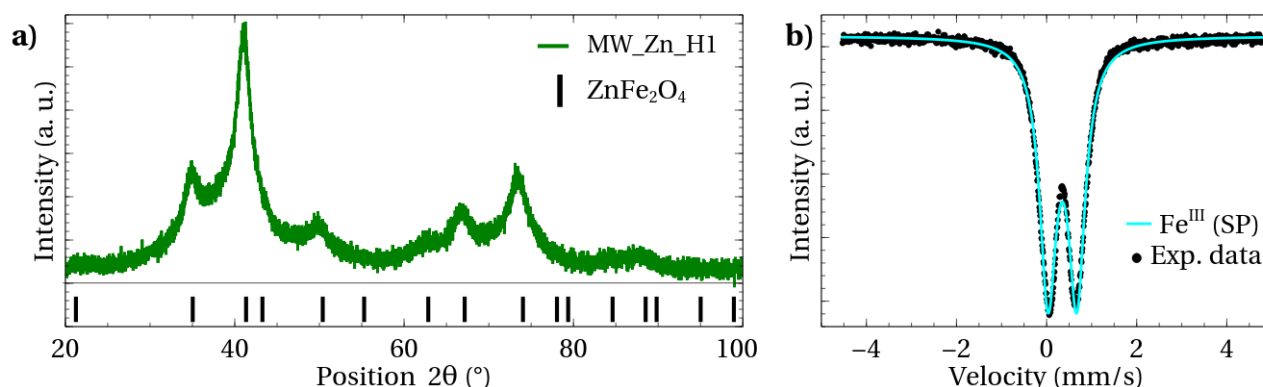


Figure 1 Prepared zinc ferrite MW_Zn_H1 (a) XRD pattern (b) ⁵⁷Fe Mössbauer spectroscopy

Room temperature transmission ⁵⁷Fe Mössbauer spectroscopy revealed only superparamagnetic nanoparticles containing Fe^{III} (doublet spectral component) in **Figure 1b**. Generally, the size of superparamagnetic nanoparticles is under 20 nm. The detailed parameters of Mössbauer spectral components are included in **Table 2**.

Table 2 Components and parameters of Mössbauer spectra of prepared zinc ferrite

Sample	Component	δ ± 0.01 (mm/s)	ΔE_Q ± 0.01 (mm/s)	B_{hf} ± 0.3 (T)	FWHM ± 0.01 (mm/s)	RA ± 1 (%)	Identification
MW_Zn_H1	Doublet	0.35	0.60	---	0.46	100	Fe ^{III} (SP)

δ is the isomer shift (related to α -Fe calibration foil at room temperature), ΔE_Q is the quadruple splitting energy, B_{hf} hyperfine magnetic field and RA is relative area.

The element composition was evaluated by EDS, it identified peaks, that belongs to silicon, iron, copper, oxygen, zinc and carbon and the amount of individual elements are listed in **Table 3**. The spectrum has identified high intensity peaks, because the peaks of copper have low intensity they are not marked in **Figure 2**. The amount of iron, zinc and oxygen meet the synthetic procedure expectations, i. e. the ratio of Fe : Zn is approximated to 2 : 1.

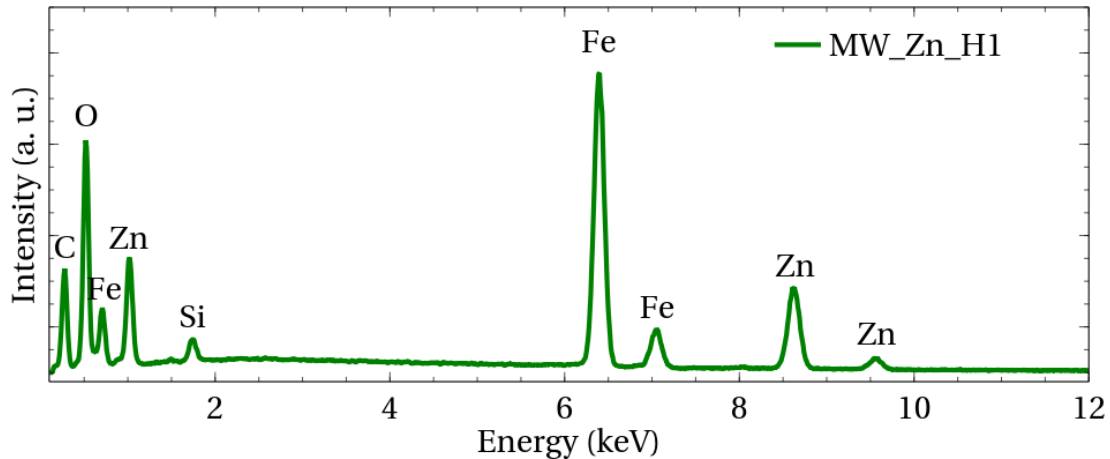


Figure 2 EDS spectrum of prepared zinc ferrite

Table 3 Quantification of EDS spectra of prepared zinc ferrite in weight % with incertenity 0.5 %

Sample	Fe	Zn	Si	C	O	Cu
MW_Zn_H1	6.5	3.1	0.5	43.0	46.8	0.1

3.2. Covering layers characterisation

The CL20ES sample plates with covering layer were analysed using conversion ^{57}Fe Mössbauer spectroscopy to obtain information about the surface phase composition. The investigation of layers was performed with a CEMS. The obtained spectra has 2 spectral components, a singlet is austenite, a doublet corresponding to zinc ferrite (**Figure 3**). The ferrite at the layers has different parameters as compared to the original spinel ferrite. The Zn_Et_200 doublet has similar parameters as untreated ferrite, but a higher temperature leads to a slight modification in the structure as presented in **Table 4**.

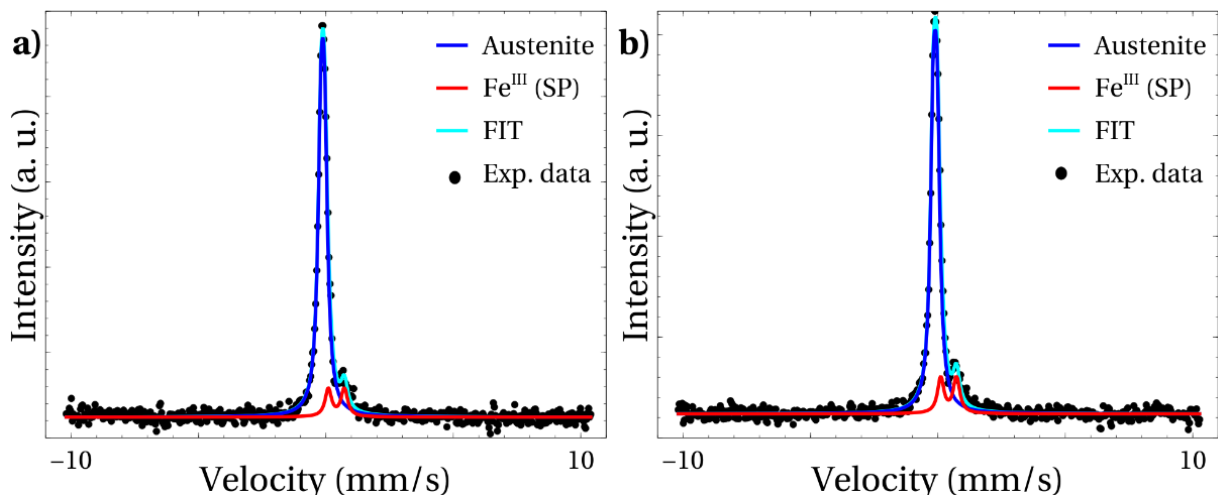


Figure 3 CEMS spectra of samples (a) Zn_Et_200 (b) Zn_Et_400

Table 4 Components and parameters of CEMS spectra of plates covered with prepared zinc ferrite

Sample	Component	δ ± 0.02 (mm/s)	ΔE_Q ± 0.02 (mm/s)	B_{hf} ± 0.3 (T)	FWHM ± 0.02 (mm/s)	RA ± 2 (%)	Identification
Zn_Et_200	Doublet 1	-0.13	0.14	---	0.28	89	Austenite
	Doublet 2	0.41	0.63	---	0.30	11	Fe ^{III} (SP)
Zn_Et_400	Doublet 1	-0.11	0.15	---	0.27	86	Austenite
	Doublet 2	0.52	0.63	---	0.30	14	Fe ^{III} (SP)

δ is the isomer shift (related to α -Fe calibration foil at room temperature), ΔE_Q is the quadruple splitting energy, B_{hf} hyperfine magnetic field and RA is relative area.

Hardness tests performed on each side of each plate show an improvement in hardness as indicated in **Table 5** with the respective conditions of preparation.

Table 5 Improvement in hardness of prepared covering layers compared to untreated sides

Sample	Alcohol	Temperature (°C)	Improvement in hardness (%)
Zn_Et_200	Ethanol	200	8.6
Zn_Et_400	Ethanol	400	9.4

4. CONCLUSION

The detailed composition of the prepared zinc ferrite is provided including phase and elemental composition. The fabrication of the covering layer on a CL20ES plate was successful as demonstrated in the result section by phase composition and hardness test. The results indicate improved hardness in all cases, in addition the relative hardness is even higher as the annealing temperature is higher. CEMS provided very useful information about the surface. The study revealed a need for covering layers not only to enhance mechanical properties, but also to passivate the surface. Spinel ferrites can be considered a good candidate to provide higher hardness and chemical stability to mechanical parts even in the case of alloy steel, which is considered as stainless.

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